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THE PREPARATION AND MAGNETIC AND STRUCTURAL EXAMINATION OF MONO--ETC(U)
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TECHNICAL REPORT NO. 5

The Preparation and Magnetic and Structural Examination
of Monomeric, Dimeric, and Polymeric Adenine Complexes of Copper(II)

by

David B. Brown^{1a}, James W. Hall^{1b}, Howard M. Helis^{1b}, Erick G. Walton,^{1a}
Derek J. Hodgson^{1b}, and William E. Hatfield^{1b}

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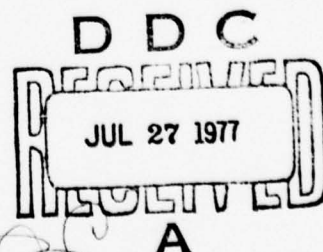
University of Vermont
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Under acidic aqueous conditions, reaction of adenine with copper(II) yields monomeric $(AdH_2^{2+})_2CuCl_6$, dimeric $(Ad)_2CuCl_4$, and linear chain polymeric $(AdH_2^{2+})_nCuCl_4$, as well as the previously reported trimeric $(AdH_2^{2+})_3CuCl_4 \cdot 4H_2O$. The crystal structure of $(AdH_2^{2+})_2CuCl_4$ is analogous to that of $(AdH_2^{2+})_2CuBr_4$. The chloro analogue crystallizes in the space group $C2/c$ of the monoclinic system with the cell dimensions being $a = 13.117(4)$,		

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(20. Abstract (continued))

$b = 8.576(1)$, $c = 11.814(4)$ Å and $\beta = 114.29(1)^\circ$ with $Z = 4$. The copper atom is roughly tetrahedrally coordinated and lies on a crystallographic two-fold axis with the four coordination sites being occupied by two chloride ligands with a Cu-Cl distance of $2.228(1)$ Å and by the N(9) atoms of two adeninium cations with a Cu-N(9) distance of $2.012(2)$ Å. The cationic purine is protonated at N(1) and N(7). There are weak Cl...Cl interactions of length $3.755(2)$ Å which link the monomeric units into zig-zag polymeric chains with a Cu-Cl...Cl angle of $169.23(7)^\circ$. The corresponding Br...Br contacts are calculated to be 3.791 Å. These ligand-ligand contacts support Heisenberg linear chain antiferromagnetism with $J(\text{Cl}) = -7.6/\text{cm}^{-1}$ and $J(\text{Br}) = -36.5/\text{cm}^{-1}$. The exchange coupling constant observed for dimeric $(\text{Ad})\text{CuCl}_2$ is $-32/\text{cm}^{-1}$.

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Introduction

Within the past decade there have been extensive studies of the interactions which occur between various transition metals and purine bases. These studies have been motivated in large part by the biological relevance of metal binding to DNA constituents. We have recently initiated investigations of the preparation and nature of such complexes specifically with copper(II), with emphasis on preparations in acidic solution. These conditions have been chosen for two principal reasons. First, purines can undergo a variety of acid-base reactions, and thus offer the possibility of coordination as neutral and also as both anionic or cationic ligands. Since there have been relatively few metal complexes characterized involving cationic ligands, preparations in acidic solutions may lead to new examples of this structure type, and hence to a greater understanding of the role of charge in metal-ligand bond formation. Secondly, we have been interested in magnetic exchange interactions in ligand-bridged copper(II) complexes, and several examples of compounds of this type are formed with purines. Although it has proven possible to correlate structure and magnetic properties in hydroxo-bridged copper(II) dimers², similar correlations have not proven possible in chloride-bridged systems, in large part because of the absence of suitably characterized materials. Reaction of guanine with copper(II) chloride in hydrochloric acid solution produced the chloride-bridged dimer trichloroguaniniumcopper(II) hydrate³, in which exchange interactions have been characterized⁴. We believed that analogous materials might be prepared using other purine bases, and these materials may allow us to extend the range of properties displayed by chloride-bridged copper(II) dimers.

In this paper we report the results of our studies on the interaction of copper(II) chloride with adenine in hydrochloric acid solutions. Depending on the specific conditions used, four distinct copper-adenine complexes may be prepared. One of these materials has been mentioned briefly in the literature, but has not been characterized, and our data permit us to suggest a structure for it. The linear trimeric complex octachlorobis(adeninium)tricopper(II) tetrahydrate has been the subject of a previous report.⁵

Experimental

Preparations: Adenine was obtained from Sigma Chemical Co. and was used as received. Octachlorobis(adeninium)tricopper(II) tetrahydrate was prepared as previously described.⁵ Because such a variety of complexes could be formed under identical, or only slightly different, reaction conditions, it became difficult to prepare pure materials, and such preparations generally required careful fractional crystallizations. Although these complexes were all prepared under several sets of conditions, the preparative details which follow appear to be those which provide the complexes most readily in pure form.

Dichloroadeninecopper(II), (Ad)CuCl₂⁶. 1.35 g. (10 mmoles) of adenine was dissolved in 12.0 ml. of 1.0 M HCl at reflux. A hot solution of 2.35 g. (14 mmoles) CuCl₂·2H₂O in 15 ml. H₂O was added. A mustard-colored precipitate began to form within a few minutes. This was collected on a sintered glass frit and washed with 1.0 M HCl. Boiling until the solution volume was ca. 15 ml. produced a further crop of product. Yield: 0.55 g (2 mmoles; 20%) Anal. Calc'd for (C₅N₅H₅)CuCl₂: C, 22.28; H, 1.87; Cl, 26.30; Cu, 23.57. Found: C, 22.07; H, 1.78; Cl, 26.26; Cu, 22.98. The solid does not melt, nor exhibit any sign of decomposition, below 265°C.

Bis(adeninum-H₂⁺²)hexachlorocuprate(II), (AdH₂⁺²)₂CuCl₆. 1.0 g (7 mmoles) adenine and 2.0 g (11 mmoles) CuCl₂·2H₂O were dissolved in 55 ml. of refluxing, concentrated HCl. Upon cooling, green crystals of product formed. These were collected on a sintered glass funnel, and washed with concentrated HCl and acetone. Yield, 0.45 g (0.8 mmole, 23%). Anal. Calc'd for (C₅N₅H₇)₂CuCl₆: C, 21.82; H, 2.56; Cl, 38.63; Cu, 11.54. Found: C, 21.78; H, 2.37; Cl, 37.85;

Cu, 11.55. Melting point: ca. 185°C darkens to brown, ca. 210-250°C melts with decomposition.

Dichlorobis(adeninium)copper(II) chloride $[\text{CuCl}_2(\text{AdH}^+)_2]\text{Cl}_2$. 0.4 g (3 mmol) adenine and 0.52 g (3 mmol) $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ were heated to boiling in 10 ml. of 6M HCl. Upon cooling to room temperature and standing for one day, bright emerald green crystals were deposited. These were collected on a sintered glass funnel and washed with 3M HCl and acetone. Yield, 0.23 g (0.5 mmol, 52%). This complex was also prepared by recrystallization of octachlorobis(adeninium)tricopper(II) tetrahydrate. 1.0 g (1.2 mmol) of $(\text{AdH}^+)_2\text{Cu}_3\text{Cl}_8 \cdot 4\text{H}_2\text{O}$ was dissolved in 20 ml. of 3M HCl at reflux. Upon cooling to 4°C for 3 days, 0.55 g (1.15 mmol, 94%) of crystalline product was deposited. Anal. Calc'd for $(\text{C}_5\text{N}_5\text{H}_6)_2\text{CuCl}_4$: C, 25.15, H, 2.53; Cu, 13.30. Found: C, 25.18; H, 2.61; Cu, 13.20. Melting point: ca. 230°C darkens, 255°C melts with decomposition.

Dibromobis(adeninium)copper(II) bromide, $(\text{AdH}^+)_2\text{CuBr}_4$ or $[\text{CuBr}_2(\text{AdH}^+)_2]\text{Br}_2$.

Although this material has been reported previously¹⁰, preparative details were not given, and for that reason we include our results. 0.40g. (3.0 mmol) of adenine were dissolved in 10 ml. of hot 3M HCl, and 0.30 g (1.35 mmol) of CuBr_2 were added. The solution was heated to boiling, then cooled to room temperature. The dark reddish purple crystals which formed were collected on a sintered glass funnel, washed with 3M HBr, and vacuum dried. Yield: 0.8 g (1.22 mmol, 90%) Anal. Calc'd for $(\text{C}_5\text{N}_5\text{H}_6)_2\text{CuBr}_4$: C, 18.32; N, 1.85; H, 2.13; Cu, 9.69. Found: C, 18.19; H, 1.56, N, 21.28; Cu, 9.52.

Micro-analyses were by Integral Microanalytical Laboratories, Inc.
Raleigh, N. C.

Magnetic Measurements. Magnetic susceptibility measurements were made on powdered samples of the complexes using a Foner-type vibrating-sample magnetometer⁷ operating at 10 kg as described elsewhere.⁸ Nickel metal was employed as a susceptibility standard. Measurements were made in the temperature range 2-155°K. The temperatures were measured with a calibrated GaAs diode. Susceptibilities were corrected for the diamagnetism of the substituent atoms using Pascal's constants⁹ and for the temperature-independent paramagnetism, N_A , of copper(II) (estimated to be 60×10^{-6} cgsu/Cu atom). Low frequency ($500-100\text{ cm}^{-1}$) infrared spectra employing Nujol mulls on polyethylene plates were obtained using a Digilab FTS-14 FT interferometer.

Crystallographic Experiments on $[\text{Cu}(\text{AdH}^+)_2\text{Cl}_2]\text{Cl}_2$. Weissenberg and precession photographs indicated that the complex is isomorphous with the analogous bromo complex,¹⁰ with four formula units in space group C2/c of the monoclinic system. The cell constants, determined by least-squares methods, are $a = 18.117(4)$, $b = 8.576(1)$, $c = 11.814(4)$ Å and $\beta = 114.29(1)^\circ$; these observations were made at 21°C with $\text{MoK}\alpha$ radiation and $\lambda(\text{MoK}\alpha)$ assumed as 0.7093 Å.

Diffraction data were collected from a prismatic crystal which was mounted roughly parallel to the (401) direction. The data were collected on a Picker four-circle diffractometer using $\text{MoK}\alpha$ radiation. The takeoff angle was 1.1° ; at this angle the peak intensity of a typical strong reflection was approximately 95% of its maximum value. A total of 4792 reflections (including standards and some Friedel pairs) was examined by the θ - 2θ scan technique at a scan rate of $1.0^\circ/\text{min}$. Care was made for both the presence of $\text{K}\alpha_1$ and $\text{K}\alpha_2$ radiations, the peaks being scanned from -0.75° in 2θ below the calculated $\text{K}\alpha_1$ peak position to $+0.75^\circ$ in 2θ above the calculated $\text{K}\alpha_2$ peak position. Stationary-counter, stationary-crystal background counts of 10 sec were taken at each end of the scan.

A unique data set having $2\theta < 65^\circ$ was gathered. There were few reflections above background at values of $2\theta > 65^\circ$. Throughout the data collection, the intensities of three standard reflections, measured every 100 reflections, remained essentially constant.

Data processing was carried out as described by Corfield, *et al.*¹¹ After correction for background the intensities were assigned standard deviations according to the formula¹¹

$$\sigma(I) = [C + 0.25(t_s/t_b)^2(B_H + B_L) + (pI)^2]^{1/2}$$

with the value of p chosen to be 0.05. The values of I and $\sigma(I)$ were corrected for Lorentz-polarization effects but not for absorption. The

absorption coefficient for the sample with Mo radiation is 19.7 cm^{-1} , and for the sample used a trial calculation suggested that the maximum effect of absorption is less than 5% (on F^2) in any intensity. A total of 4792 reflections was collected, of which 2156 were independent data with $I > 3\sigma(I)$; only these data were used in the final refinement of the structure.

Inspection of a three-dimensional Patterson function¹² demonstrated that the complex was indeed isostructural with the bromo analog. A least-squares calculation including all non-hydrogen atoms with anisotropic thermal parameters converged to values of the conventional R-factors¹³ of 0.050 and 0.072. The hydrogen atoms were located in a difference Fourier map, and a least-squares calculation in which non-hydrogen atoms were refined anisotropically while hydrogen atoms were refined isotropically gave $R_1 = 0.042$ and $R_2 = 0.054$.

Examination of the values of $|F_c|$ and $|F_o|$ suggested that the data were suffering from secondary extinction, so a correction of the type described by Zachariasen¹⁴ was applied. Least-squares refinement led to a value of the extinction coefficient of $5.1(8) \times 10^{-8}$; this small change in the model brought about only an insignificant change in the values of R_1 and R_2 .

Examination of the values of $|F_c|$ and $|F_o|$ suggested to us that no correction for secondary extinction is necessary, and none was applied. In the final cycle of least-squares refinement, there were 2156 observations and 139 variables, a reflection to variable ratio of 15.5 : 1. In this final cycle, no parameter underwent a shift of more than 0.04σ , which is taken as evidence of convergence. The value of R_2 shows no unusual dependence on $|F_o|$ or on $\sin\theta$, which suggests that our weighting scheme is adequate. A final difference Fourier showed no peaks higher than $0.6 \text{ e}\text{\AA}^{-3}$. The positional and thermal parameters derived from the final cycle, along with their standard deviations as estimated from the inverse matrix, are presented in Tables I

and II. A compilation of observed and calculated structure amplitudes is available.¹⁵

Description of the Structure. The structural analysis was undertaken in large part because the observed magnetic properties (*vide infra*) are apparently inconsistent with the monomeric description given by other workers for the bromo analog.¹⁰ A view of the coordination around a single copper atom is given in Figure 1; it is apparent that the geometry of this complex is very similar to that of the bromo complex. The copper atom lies on a crystallographic two-fold axis, the four coordination sites being occupied by two chloride ligands and the N(9) atoms of two adeninium cations. The Cu-Cl and Cu-N(9) distances of 2.228(1) and 2.012(2) Å, respectively are normal, the latter value being comparable to the value of 2.013(5) Å in the bromo complex¹⁰ and to values of 1.995 to 2.041 Å reported for a variety of other Cu-adenine complexes.¹⁶ The Cl-Cu-Cl, Cl-Cu-N, N-Cu-N, and two independent bond angles subtended at copper by the coordinated ligands are 97.78(5)°, 93.8(1)°, 94.74(7)° and 144.66(7)°, respectively; these compare with values of 95.81(5)°, 95.1(2)°, 95.1(2) and 144.7(2)°, respectively, in the bromo complex.

The cationic purine is protonated at N(1) and N(7), as expected for an adenine complex with N(9)-coordination. The geometry of the ligand is normal, the internal angles at N(1) and N(7) showing the large values of 123.7(2)° and 106.8(2)°, respectively, as a consequence of their being protonated; as has been noted by Ringertz,¹⁷ these values are larger than those observed at these atoms when they are unprotonated. The internal bond angle at N(9) of 105.0(2) is, similar to that found for unprotonated N(9) in purines; this is consistent with the observation of Hodgson¹⁶ that metal ion coordination

brings about little or no change in the internal angles of purines relative to their unsubstituted values. The bond lengths and angles in the cation are listed in Tables 3 and 4, respectively.

There is no other close approach of any atom to the copper center. As is seen in Figure 2, however, there are weak Cl...Cl interactions of length 3.755(2) Å which link one copper center to those above and below it to form infinite zig-zag polymeric chains with a Cu-Cl...Cl "bond" angle of 169.23(7)°. While these Cl...Cl separations might normally be considered large [the van der Waals radius of Cl is given by Pauling¹⁸ as 1.80 Å], Hatfield and Jones¹⁹ have shown that Cl...Cl separations of 4.11 Å are apparently adequate to provide a pathway for magnetic exchange between nominally monomeric $[\text{CuCl}_5]^{3-}$ anions in the crystals of $[\text{Co}(\text{NH}_3)_6][\text{CuCl}_5]$. Hence, the present arrangement of $[\text{Cu}(\text{AdH}^+)\text{Cl}_2]^{2+}$ "monomers" would also be expected to provide such a pathway, and this is evidently the case (*vide infra*). In the bromo analog, we calculate that the corresponding Br...Br separation is 3.791 Å. Since this value is only 0.04 Å larger than that in the chloro complex, while the van der Waals radius of Br is 0.15 Å larger¹⁸ than that of Cl, one would anticipate that the magnetic coupling in the bromo complex would be greater than that in the chloro complex; this expectation is again consistent with our observations (*vide infra*).

Results and Discussion

The numbering scheme commonly used for adenine (6-aminopurine) is shown in Figure 1. For such a multifunctional system, it is to be expected that a variety of different types of coordination behavior toward transition metals may be found, and this has been confirmed experimentally. The structures of metal complexes of purine and pyrimidine bases have been reviewed recently.¹⁶ In the specific case of copper(II), complexes involving neutral, cationic, and anionic adenine are known, as are complexes involving both monodentate and bidentate adenine. The complex of composition $\text{Cu}(\text{Ad-H}^-)_2 \cdot 4\text{H}_2\text{O}$ contains the dimeric unit $\text{Cu}_2(\text{Ad-H}^-)_4(\text{H}_2\text{O})_2$.²⁰ This dimer has a structure similar to that of copper acetate, with four bridging adenine anions, coordinated through N3 and N9, and water occupying axial sites on copper. Two complexes of neutral adenine, $\text{Cu}(\text{Ad})_2(\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ ²¹ and $\text{Cu}(\text{Ad})_2\text{Cl}_2 \cdot 3\text{H}_2\text{O}$ ²², have similar dimeric structures, involving bridging adenine (N3 and N9) and water or chloride, respectively, occupying the axial sites. Strong magnetic exchange interactions, comparable to those observed in copper acetate, have been demonstrated in all of these compounds²³⁻²⁶. Unidentate coordination of neutral adenine (via N9) has also been demonstrated in the complex $[\text{Cu}(\text{glygly})(\text{Ad})\text{H}_2\text{O}]$, where glygly = glycylglycinato.²⁷ In complexes of 9-methyladenine, where the favored site of coordination is blocked, the ligand coordinates to copper in unidentate fashion via N7^{16,28}.

Two complexes involving protonated adenine coordinated to copper(II) have been characterized. The unique trimeric complex $(\text{AdH}^+)_2\text{Cu}_3\text{Cl}_8 \cdot 4\text{H}_2\text{O}$ involves both adeninium and chloride bridges between the central and terminal copper(II) sites²⁹, and we have recently characterized the magnetic exchange in this complex.⁵ $[\text{Cu}(\text{AdH}^+)_2\text{Br}_2]\text{Br}_2$ involves unidentate coordination of protonated

adenine. In this complex the copper atom is coordinated to two bromide ions and to the N9 atoms of two AdH^+ ligands, giving a geometry at Cu(II) best described as tetrahedrally-distorted square-planar.¹⁰ We shall comment on the magnetic properties of this compound and this structure in more detail when we discuss the stoichiometrically and structurally-related complex $[\text{Cu}(\text{AdH}^+)_2\text{Cl}_2]\text{Cl}_2$.

The adenine complexes which were studied in this work are discussed individually in the following sections. In most cases, the magnetic and spectroscopic data obtained allow us to postulate reasonable structures for them.

(Ad)CuCl₂. This complex, prepared in solutions which are only slightly acidic, contains neutral adenine as a ligand. This is, of course, required by the empirical formula, and is confirmed by the lack of reactivity with water, in contrast to materials containing the adeninium cation. Although this complex has been reported previously,³⁰ there has been little characterization of it, and no structure has been suggested. The magnetic susceptibility of (Ad)CuCl₂ exhibits a maximum at 55°K, and the complex is diamagnetic below 10°K. The form of the susceptibility is typical for exchange coupled copper dimers, and the data may be accurately approximated using the Bleaney-Bowers equation (1)³¹

$$\chi_m = \frac{Ng^2\beta^2}{3kT} [1 + 1/3 \exp(-2J/kT)]^{-1}. \quad (1)$$

The best least-squares fit of the data to this equation gives a singlet-triplet splitting, $2J$, of -64 cm^{-1} with $g = 2.08$. These values are in good agreement with those previously found²⁵ for this material, those parameters being $2J = -61 \text{ cm}^{-1}$ and $g = 2.10$.

On the basis of this data we propose the structure shown in Figure 3. The magnetic results clearly demonstrate the presence of exchange coupled copper(II) dimers, and thus a ligand-bridged structure is required. Given the proclivity of copper(II) to attain coordination numbers greater than four, and the coordinative unsaturation implied by the formula, it is likely that adenine functions as a bidentate ligand. In accord with previous structural results on copper-adenine complexes, then, we propose that adenine serves as a bridging ligand in this complex. The magnitude of the exchange integral, $J = -32 \text{ cm}^{-1}$, is consistent with this assignment. The value of J in $(\text{AdH}^+)_2\text{Cu}_3\text{Cl}_8 \cdot 4\text{H}_2\text{O}$, with a single adenine bridge between copper sites, is -16 cm^{-1} .⁵ Since the magnitude of J should be proportional to the number of bridging ligands involved in the superexchange interaction, a structurally similar complex with two adenine bridges is then predicted to have a value of J near -32 cm^{-1} , in excellent accord with our results. Our evidence for the chloride bridges in the proposed structure is somewhat more tenuous, but is consistent with experimental data. First, an absorption in the infrared spectrum at 268 cm^{-1} is in the range observed for bridging chloride in copper complexes.³² The value of J is also consistent with a structure involving bridging chloride. As previously noted,⁵ copper dimers involving only adenine or adenine anion bridges have values of J (per adenine) in the range -20 to -35 cm^{-1} , and in such complexes the copper-copper distance is approximately 3.0 \AA .¹⁶ In $(\text{AdH}^+)_2\text{Cu}_3\text{Cl}_8 \cdot 4\text{H}_2\text{O}$, which has J somewhat lower than this range, the copper-copper distance is much longer, 3.48 \AA .²⁹ This longer distance is presumably the result of the bridging demands set by the chloride ion, since copper-copper distances in a variety of chloride-bridged copper dimers fall in the range 3.37 - 4.41 \AA .³³ The similarly low value of J

observed for $(\text{Ad})\text{CuCl}_2$ may then suggest structural constraints similar to those in $(\text{AdH}^+)_2\text{Cu}_3\text{Cl}_8 \cdot 4\text{H}_2\text{O}$, and, in consequence, bridging chloride ions.

As in the case of $(\text{AdH}^+)_2\text{Cu}_3\text{Cl}_8 \cdot 4\text{H}_2\text{O}$, it is possible that the dimeric unit in $(\text{Ad})\text{CuCl}_2$ is polymerized via bridging chloride ions into a chain structure. Although there is no direct evidence to suggest such association, the low solubility of this complex, in contrast to the tetra- μ -adenine dimers, is compatible with polymerization.

$(\text{AdH}_2^{2+})_2\text{CuCl}_6$. Reaction of adenine and copper(II) in concentrated HCl solution produces a material containing the diprotonated adenine moiety. This is, to our knowledge, the first report of this ion. Given both the excess of potential ligands and the much lower basicity expected for diprotonated adenine, it is likely that AdH_2^{2+} is not coordinated to copper in this material. For the same reasons, it is expected that monomeric chlorocuprates, $\text{CuCl}_x^{(2-x)-}$, will be present. The lack of exchange interactions, hence the presence of monomeric copper complexes, is clearly reflected in the magnetic susceptibility. Over the temperature range 0-50°C $(\text{AdH}_2^{2+})_2\text{CuCl}_6$ exhibits Curie-law behavior, and the temperature independent magnetic moment, $\mu_{\text{eff}} = 1.74 \text{ B.M.}$, implies monomeric copper species.

There is little precedent in the literature for species containing " CuCl_6^{4-} ". Recently, however, a similar material was reported with the piperazinium dication, and based on electronic and infrared spectra was assigned as containing a square-planar CuCl_4^{2-} ion.³⁴ Based on the similarities in color and formula, it is tempting to assign a similar structure to $(\text{AdH}_2^{2+})_2\text{CuCl}_6$, although the possibility of higher coordination numbers at

copper can not be ruled out. $(\text{PiperazineH}_2^{2+})_2\text{CuCl}_6$ is thermochromic,³⁴ undergoing a reversible color change when heated to 90°C, a change attributed to a conversion toward tetrahedral geometry. $(\text{AdH}_2^{2+})\text{CuCl}_6$ does not exhibit such thermochromic behavior, although one interesting color phenomenon was observed. Some preparations of this complex led to an apparent mixture of yellow and green crystals. However, under microscopic examination there were found to be not only yellow crystals and green crystals, but also what appeared to be well formed crystals which were yellow at one end and green at the other. Although the yellow color seemed to slowly convert to green over a period of several months, these mixed crystals were otherwise rather stable.

Although the nominal excess of available ligands leads to monomeric copper complexes in this particular case, the existence of " CuCl_6^{4-} " is no guarantee of monomeric behavior. The complex $[\text{Co}(\text{en})_3]\text{CuCl}_5 \cdot \text{H}_2\text{O}$ was found to contain the $[\text{Cu}_2\text{Cl}_8]^{4-}$ ion³⁵, and we have prepared a " CuCl_6^{4-} " salt which, based on magnetic susceptibility, is clearly dimeric.³⁶

$(\text{AdH}^+)_2\text{CuCl}_4$. This bright green, crystalline complex has been prepared both directly from the reaction of adenine and copper chloride in 6M HCl, and by the recrystallization of $(\text{AdH}^+)_2\text{Cu}_3\text{Cl}_8 \cdot 4\text{H}_2\text{O}$ from 3M HCl. This material is analogous to the known bromide compound (*vide supra*).

A plot of the magnetic susceptibility of $(\text{AdH}^+)_2\text{CuCl}_4$ as a function of temperature in the interval 2-50°K is given in Figure 4. The susceptibility maximizes at 13°K, a result which provides a clear indication of magnetic exchange interactions. Initial attempts to understand these data in terms of exchange-coupled copper(II) dimers were unsuccessful, and these efforts stimulated the structural study reported therein. The data may,

however, be accurately fit by the Heisenberg formulation for exchange in an infinite chain of exchange-coupled copper ions.

The Hamiltonian for spin interaction between neighbouring paramagnetic ions along an infinite one-dimensional chain is given by equation (2),³⁷ where J is the

$$H = -2J \sum_{i=1}^N [S_{iz}S_{(i+1)z} + \gamma(S_{ix}S_{(i+1)x} + S_{iy}S_{(i+1)y})] \quad (2)$$

exchange integral and γ can have values ranging from 0 to 1. When $\gamma=1$, the isotropic Heisenberg model is the result, while for the limit $\gamma=0$ the anisotropic Ising model is obtained. Closed-form expressions for the magnetic susceptibility of a linear chain of ions of $S = 1/2$ are available for the Ising model,³⁸ while the Heisenberg model can be approximated by using the results of Bonner and Fisher³⁷ for infinite $S = 1/2$ chains where $kT_{\max}/|J| \approx 1.282$ and $|J|_{\max}/g^2 \mu_B^2 N \approx 0.0735$. The anisotropic Ising simplification of the exchange Hamiltonian (1) is substantially in error for the description of one-dimensional polymeric systems having large exchange interactions.³⁹ Furthermore, a single-crystal magnetic-susceptibility study⁴⁰ of the linear-chain complex $[\text{Cu}(\text{pyz})_2(\text{NO}_3)_2]_n$ demonstrated that, even for the small value $|J|/k = 5.3^\circ$, the exchange interaction is quite isotropic. The Heisenberg approximation was therefore chosen to describe the experimental magnetic susceptibilities of $[\text{AdH}^+]_2\text{CuCl}_2\text{Cl}_2$.

Since no closed-form expressions are available for the Heisenberg linear-chain model susceptibility, the experimental data were graphically fitted to the results of Bonner and Fisher.³⁷ The best fit obtained for the susceptibility of $(\text{AdH}^+)_2\text{CuCl}_4$ is shown as the solid line in Figure 4. The parameters obtained were $J = -7.6 \text{ cm}^{-1}$ and $g = 2.10$.

The bromide analogue has been characterized structurally,¹⁰ with the structure being described as monomeric $[(\text{AdH}^+)_2\text{CuBr}_2]^{+2}$ ions with a geometry approximately halfway between tetrahedral and square-planar. A calculation of the bromide-bromide contact reveals the same close approach (*vide supra*) found in the case of the chloro compound, and a study of the magnetic susceptibility of $[(\text{AdH}^+)_2\text{CuBr}_2]\text{Br}_2$ (see Figure 5) reveals linear chain behavior with $J = -36.5 \text{ cm}^{-1}$ and $g = 2.02$. This is a remarkable result since exchange coupling of this magnitude would not be expected for a superexchange pathway of the sort found here.

Conclusions: We have shown that under acidic aqueous conditions, reaction between adenine and copper(II) produces several complexes. These include, in addition to the previously reported linear trimer $(\text{AdH}^+)_2\text{Cu}_3\text{Cl}_8 \cdot 4\text{H}_2\text{O}$, monomeric $(\text{AdH}_2^{2+})_2\text{CuCl}_6$, dimeric $(\text{Ad})\text{CuCl}_2$, and linear-chain polymeric $(\text{AdH}^+)_2\text{CuCl}_4$. When considered in light of the previously known complexes of copper(II) with both neutral and anionic adenine, the remarkable versatility of multifunctional ligands such as adenine becomes clear.

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Supplementary Material Available: A listing of observed and calculated structure amplitudes (12 pages). Ordering information is given on any current masthead page.

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b) University of North Carolina
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6. The following abbreviations will be used throughout this paper:
Ad = neutral adenine, $C_5N_5H_5$; AdH^+ = monoprotonated adenine, $C_5N_5H_6$;
 AdH_2^{2+} = diprotonated adenine, $C_5N_5H_6$; and $ad-H^-$ = deprotonated adenine, $C_5H_5H_4$.
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Table 1

Positional Parameters in $[\text{Cu}(\text{AdH}^+)_2\text{Cl}_2]\text{Cl}_2$

<u>Atom</u>	<u>X</u>	<u>Y</u>	<u>Z</u>
Cu	0.0	-0.17052(5)	0.25
Cl(1)	0.01000(5)	-0.34770(7)	0.00334(3)
Cl(2)	0.27562(5)	0.22733(9)	0.19128(7)
N(1)	0.1421(2)	0.4207(3)	0.3355(2)
C(2)	0.1043(2)	0.3336(3)	0.2308(1)
N(3)	0.0807(2)	0.1901(3)	0.2292(2)
C(4)	0.0943(2)	0.1336(3)	0.3436(2)
C(5)	0.1329(2)	0.2151(3)	0.4533(2)
C(6)	0.1594(2)	0.3677(3)	0.4515(3)
N(7)	0.1351(2)	0.1170(3)	0.5467(2)
C(8)	0.0976(2)	-0.0144(3)	0.4924(3)
N(9)	0.0719(1)	-0.0103(2)	0.3686(2)
N(10)	0.1985(2)	-0.4559(3)	0.0506(3)
H1	0.156(2)	0.529(4)	0.327(4)
H2	0.094(2)	0.388(4)	0.150(3)
H7	0.154(2)	0.135(4)	0.621(4)
H8	0.091(2)	-0.096(4)	0.537(3)
H101	0.214(2)	0.550(5)	0.544(4)
H102	0.209(2)	0.417(5)	0.625(4)

Table 2

Thermal Parameters in $[\text{Cu}(\text{AdH}^+)_2\text{Cl}_2]\text{Cl}_2$

Atom	β_{11}^a or $B(\text{\AA}^2)$	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	0.00239(2)	0.00334(6)	0.00236(4)	0.0	0.00053(2)	0.0
Cl(1)	0.00334(3)	0.00513(8)	0.00366(6)	-0.00052(4)	0.00105(3)	0.00190(5)
Cl(2)	0.00315(3)	0.00661(9)	0.00381(5)	0.00160(4)	0.00036(3)	-0.00040(6)
N(1)	0.0025(1)	0.0036(3)	0.0049(2)	-0.0006(1)	0.0016(1)	0.0002(2)
C(2)	0.0025(1)	0.0061(3)	0.0038(2)	-0.0038(2)	0.0016(1)	0.0005(2)
N(3)	0.00240(9)	0.0056(3)	0.0027(2)	-0.0004(1)	0.0011(1)	0.0000(2)
C(4)	0.00171(9)	0.1336(2)	0.0027(2)	0.0000(1)	0.0009(1)	0.0001(2)
C(5)	0.00171(9)	0.0040(3)	0.0027(2)	-0.0001(1)	0.0008(1)	-0.0003(2)
C(6)	0.00163(9)	0.0041(3)	0.040(2)	-0.0001(1)	0.0010(1)	-0.0008(2)
N(7)	0.0025(1)	0.0053(3)	0.0020(2)	-0.0004(1)	0.0004(1)	-0.0003(2)
C(8)	0.0024(1)	0.0050(3)	0.0027(2)	-0.0004(1)	0.0007(1)	0.0005(2)
N(9)	0.00199(8)	0.0035(2)	0.0024(2)	-0.0003(1)	0.0005(1)	0.0001(1)
N(10)	0.0026(1)	0.0051(3)	0.0052(2)	0.0009(1)	0.0009(1)	0.0020(2)
H1	3.2(8)					
H2	1.8(6)					
H7	3.3(9)					
H8	2.2(7)					
H101	3.9(9)					
H102	3.0(8)					

^a The form of the anisotropic thermal ellipsoid is
 $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

Table 3

Selected Bond Lengths in $[\text{Cu}(\text{AdH}^+)_2\text{Cl}_2]\text{Cl}_2$

<u>Atoms</u>	<u>Distance</u>
Cu-Cl(1)	2.228(1)
Cu-Cl(2)	3.931(2)
Cu-N(9)	2.015(2)
Cl(1)-Cl(1)'	3.755(2)
N(1)-C(2)	1.364(4)
N(1)-C(6)	1.353(4)
C(2)-N(3)	1.301(4)
N(3)-C(4)	1.360(3)
C(4)-C(5)	1.382(4)
C(4)-N(9)	1.369(3)
C(5)-C(6)	1.397(4)
C(5)-N(7)	1.374(3)
C(6)-N(10)	1.328(4)
N(7)-C(8)	1.336(4)
C(8)-N(9)	1.340(3)
N(1)-H1	0.97(4)
C(2)-H2	1.00(3)
N(7)-H7	0.81(5)
C(8)-H8	0.91(4)
N(10)-H101	0.87(4)
N(10)-H102	0.88(4)

Table 4

Selected Bond Angles in $[\text{Cu}(\text{AdH}^+)_2\text{Cl}_2]\text{Cl}_2$

<u>Atoms</u>	<u>Angle(°)</u>
N(1)-Cu-N(1)'	93.8(1)
N(1)-Cu-Cl(1)	94.74(7)
N(1)-Cu-Cl(1)'	114.66(7)
N(1)'-Cu-Cl(1)	114.66(7)
N(1)'-Cu-Cl(1)'	94.74(7)
Cl(1)-Cu-Cl(1)'	97.78(5)
C(2)-N(1)-C(6)	123.7(2)
N(1)-C(2)-N(3)	124.8(3)
C(2)-N(3)-C(4)	113.4(3)
N(3)-C(4)-C(5)	124.6(2)
N(3)-C(4)-N(9)	125.9(2)
C(5)-C(4)-N(9)	109.5(2)
C(4)-C(5)-C(6)	120.2(2)
C(4)-C(5)-N(7)	106.3(2)
C(6)-C(5)-N(7)	133.5(2)
N(1)-C(6)-C(5)	113.1(2)
N(1)-C(6)-N(10)	121.2(3)
C(5)-N(7)-C(8)	106.8(2)
N(7)-C(8)-N(9)	112.4(2)
C(4)-N(9)-C(8)	105.0(2)
Cu-Cl(1)-Cl(1)'	169.23(7)

Figure Captions

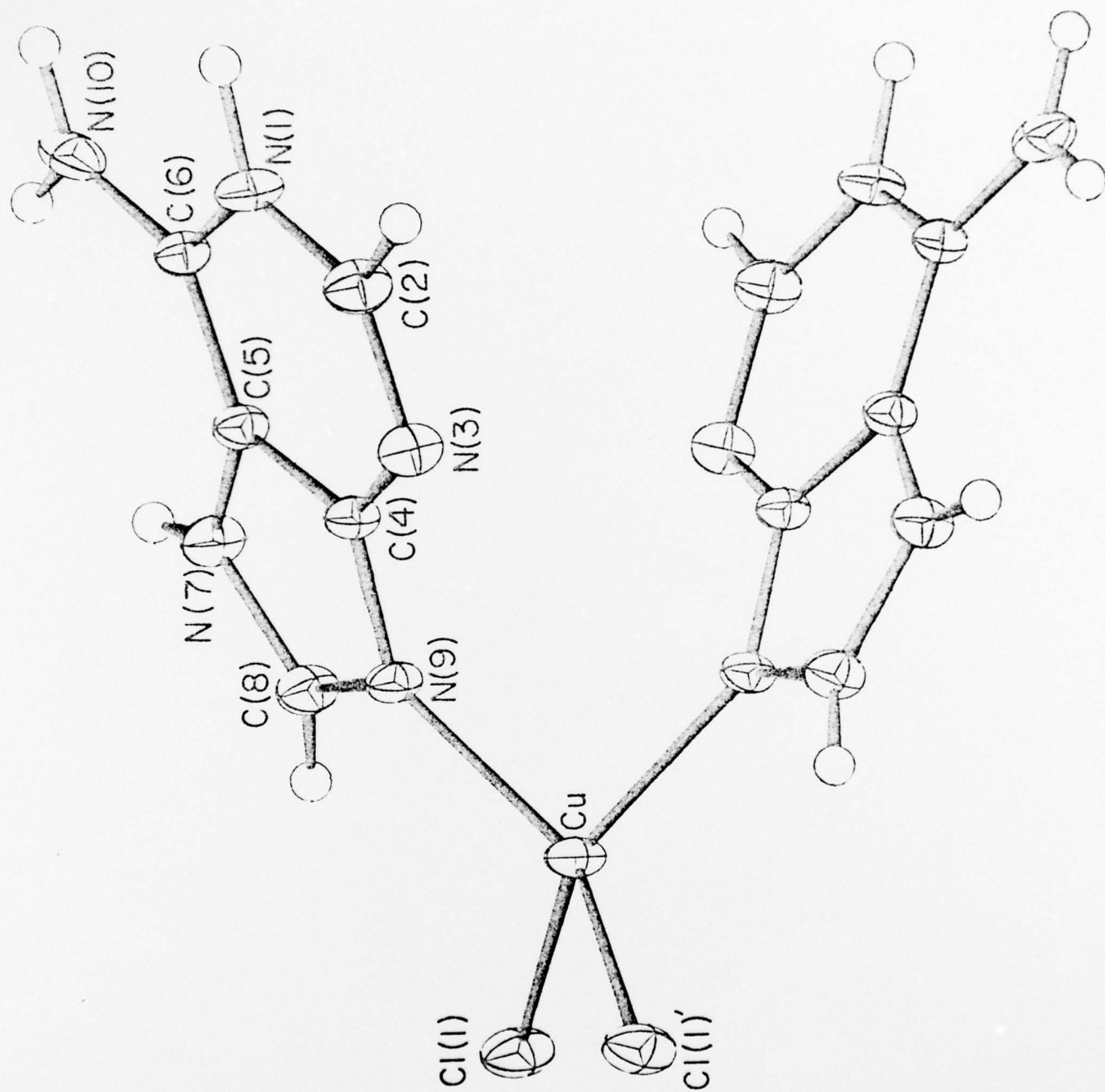
Figure 1: View of a single unit of the $[\text{CuCl}_2(\text{AdH}^+)_2]^{2+}$ cation; the hydrogen atoms are shown as spheres of arbitrary size, while anisotropic thermal ellipsoids are drawn at the 40% probability level.

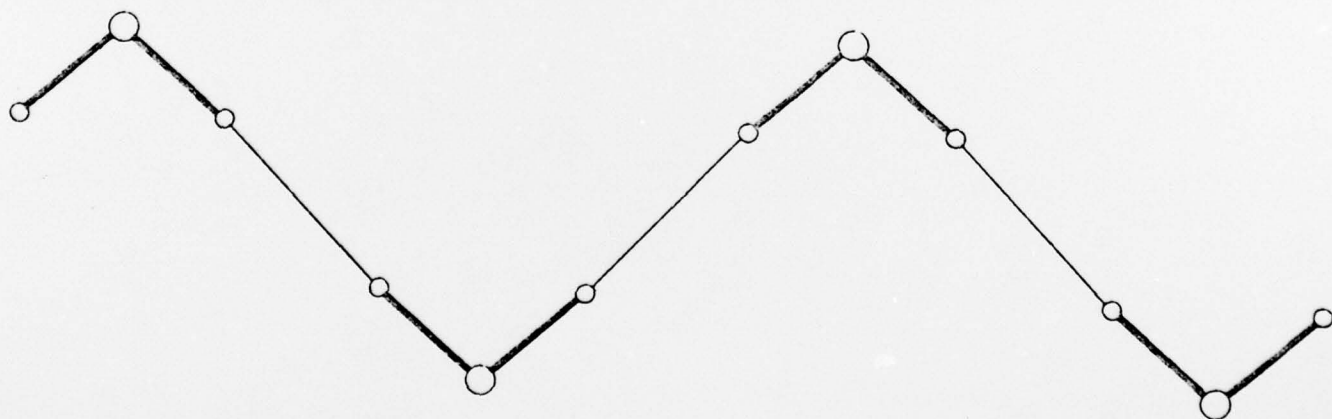
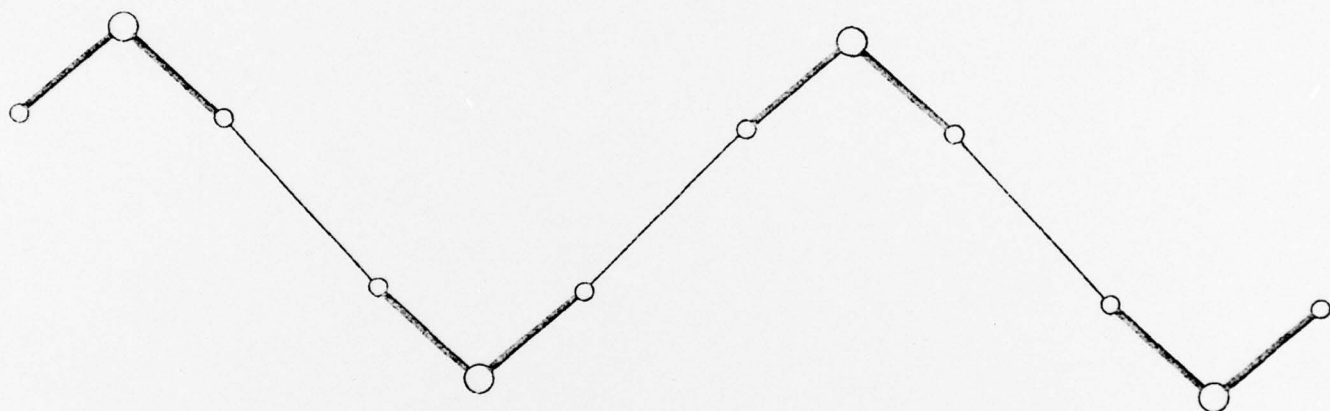
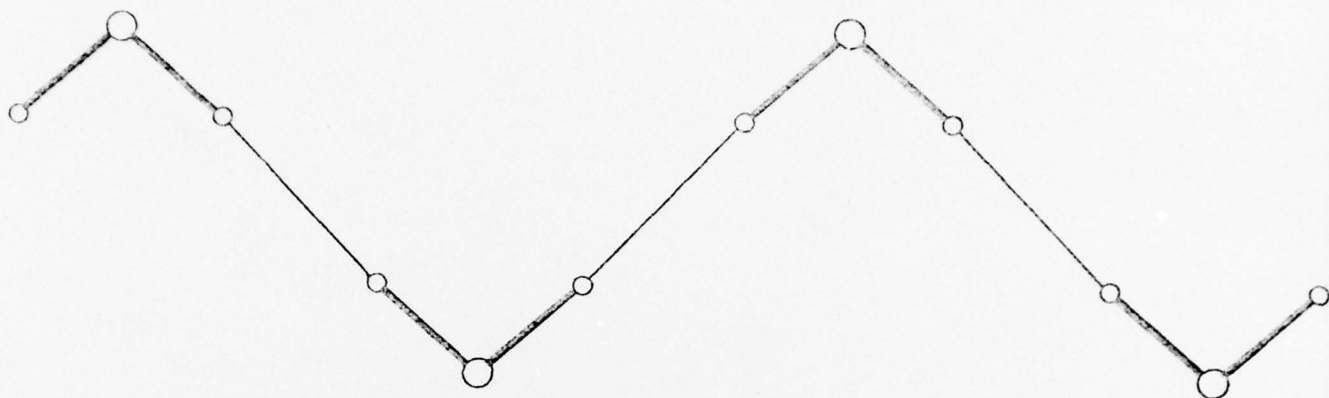
Figure 2: View of the zigzag polymeric chain interactions in the crystals of $[\text{CuCl}_2(\text{AdH}^+)_2]\text{Cl}_2$. The view direction is along the crystallographic b -axis.

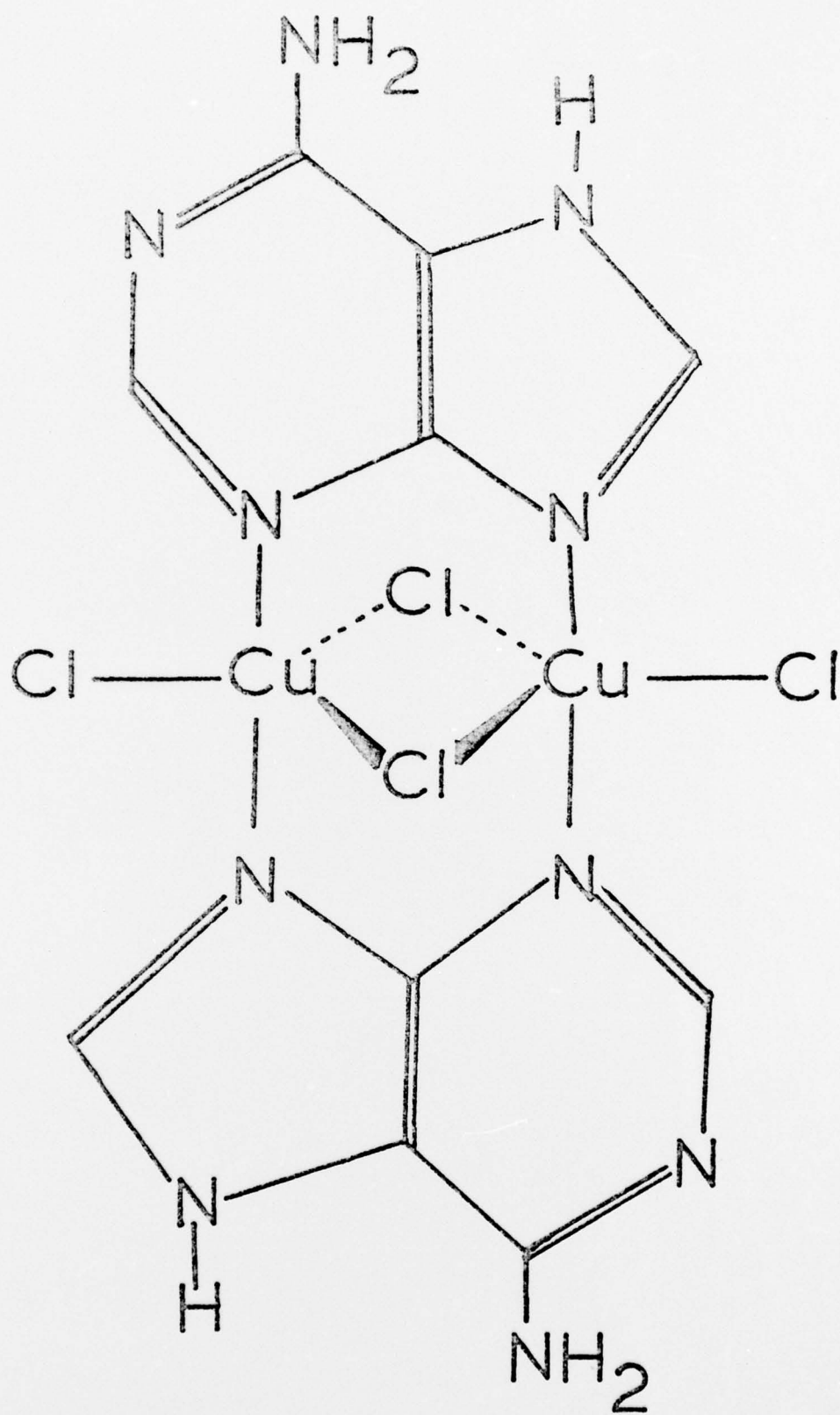
Figure 3: Proposed structure for $(\text{Ad})\text{CuCl}_2$.

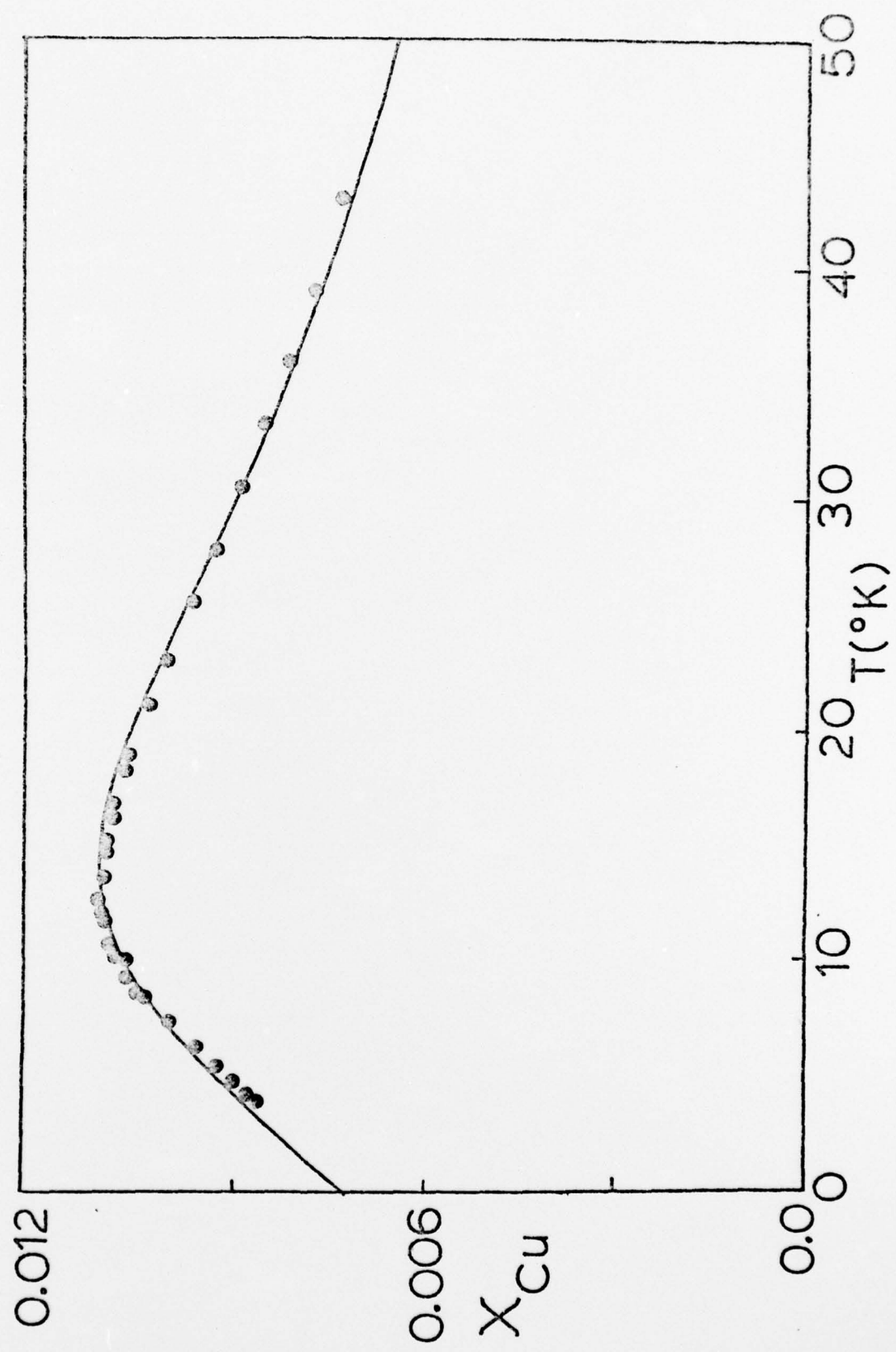
Figure 4: Experimental magnetic susceptibility per copper atom for $[\text{CuCl}_2(\text{AdH}^+)_2]\text{Cl}_2$ as a function of temperature. The solid line is the best fit to the Heisenberg linear-chain model.

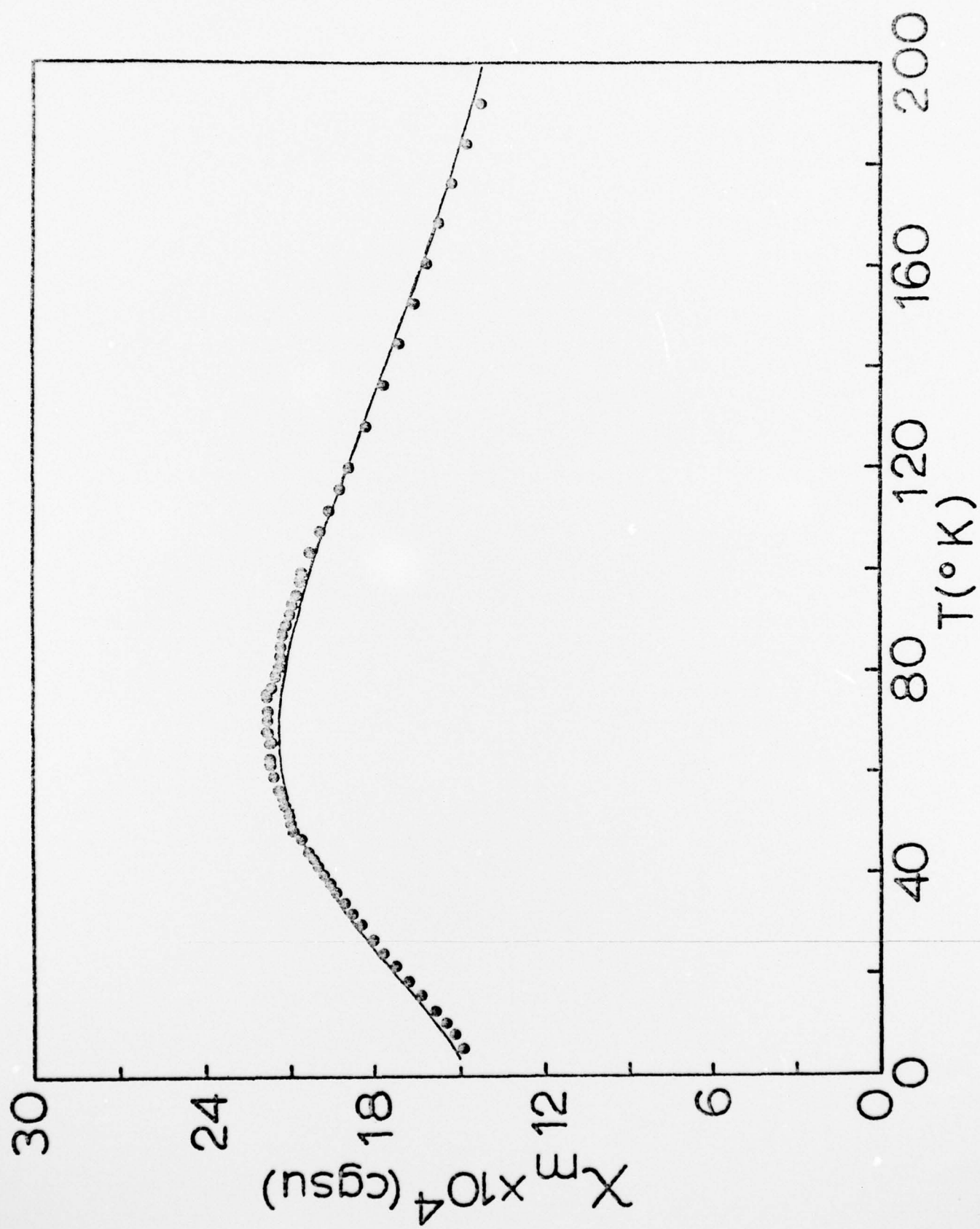
Figure 5: Experimental magnetic susceptibility per copper atom for $[\text{CuBr}_2(\text{AdH}^+)_2]\text{Br}_2$ as a function of temperature. The solid line is the best fit to the Heisenberg linear chain model.











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